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Synthesis and Ion-Binding Studies of a Platinum(II) Terpyridine Complex with Crown Ether Pendant. X-ray Crystal Structure of [Pt(trpy)(S-benzo-15-crown-5)]PF_6

Vivian Wing-Wah Yam,* Rowena Pui-Ling Tang, Keith Man-Chung Wong,* Chi-Chiu Ko, and Kung-Kai Cheung

Department of Chemistry, The University of Hong Kong,
Pokfulam Road, Hong Kong, P. R. China

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Introduction

The square planar platinum(II) system has been studied for decades because of its intriguing spectroscopic and photophysical behavior[1−3] that is partly related to the propensity of platinum(II) to form weak metal−metal interactions.[2] In recent years, platinum(II) polypyridyl complexes have been extensively investigated because of their interesting spectroscopic behavior[1c,d,g,i−k,2a,d,f−i,3] as well as their useful physical and biological properties, such as antitumor activities and binding interaction with DNA[4] and protein.[5] The recent revival of interest in crown ethers and other related inclusion compounds in molecular recognition studies and the design of molecular switches and probes,[6] together with our recent efforts[7] as well as those of others[8] in the utilization of transition metal complexes containing crown ether moieties for such work, has aroused our interest in the exploration of the platinum(II) system. To the best of our knowledge, studies on the platinum(II) crown system are rare[9] and no ion-binding studies for this class of compounds have been explored. Herein are reported the synthesis, ion-binding properties, and X-ray crystal structure of a Pt(II) terpyridyl complex with the mercaptobenzo-15-crown-5 ligand.

Experimental Section

Reagents and Materials. Dichloro(1,5-cyclooctadiene)platinum(II) and 2,2′:6′,2′′-terpyridine were obtained from Strem Chemicals Inc. 3,4-Dimethoxythiophenol was purchased from Lancaster Synthesis Ltd. [Pt(trpy)Cl]Cl·$2H_2O$[10] and 4′-mercaptomonobenzo-15-crown-5[11] were synthesized according to literature methods. All other reagents were of analytical grade and were used as received.

Synthesis. A. [Pt(trpy)(S-benzo-15-crown-5)]PF_6, 1. To a stirred solution of [Pt(trpy)Cl]Cl·$2H_2O$ (100 mg, 0.18 mmol) in deionized water (40 mL) was added 2 mL of 6 M sodium hydroxide. The resultant solution was stirred at 40 °C for 30 min. 4′-Mercaptomonobenzo-15-crown-5 (60 mg, 0.20 mmol) was then added to the reaction mixture, and the mixture was stirred for 12 h. Upon addition of tetrabutylammonium hexafluorophosphate, a purple solid was obtained that was then filtered, washed with methanol, and dried. Subsequent recrystallization by diffusion of diethyl ether vapor into an acetonitrile solution of the product gave **1** as purple crystals. Yield: 90 mg (57%). ^1H NMR (300 MHz, CD_3CN, 298 K, relative to Me_4Si): δ 3.58 (s, 8H, $-OCH_2-$), 3.70 (m, 4H, $-OCH_2-$), 3.95 (m, 4H, $C_6H_3OCH_2-$), 6.65 (d, 1H, $J = 8.8$ Hz, aromatic H on arenethiolate), 7.15 (m, 2H, aromatic H on arenethiolate), 7.65 (m, 2H, terpyridyl H's), 8.25 (m, 6H, terpyridyl H's), 8.45 (t, 1H, $J = 8.1$ Hz, terpyridyl H), 8.92 (d, 2H, $J = 5.6$ Hz, terpyridyl H's). Positive ESI-MS: m/z 727 $[M - PF_6]^+$, 1598 $[M\cdots M - PF_6]^+$. Anal. Calcd for $C_{29}H_{30}N_3O_5SPtPF_6$: C, 39.91; H, 3.44; N, 4.82. Found: C, 39.96; H, 3.43; N, 4.91.

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B. [Pt(trpy)(SC$_6$H$_4$(OMe)$_2$-3,4)]PF$_6$, 2. The procedure was similar to that for complex **1** except 3,4-dimethoxythiophenol was used in place of 4′-mercaptomonobenzo-15-crown-5 to give purple crystals of **2**. Yield: 69 mg (52%). ^{1}H NMR (300 MHz, CD$_3$CN, 298 K, relative to Me$_4$Si): δ 3.68 (d, 6H, $J = 13.2$ Hz, $-$OCH$_3$), 6.67 (d, 1H, $J = 8.8$ Hz, aromatic H on arenethiolate), 7.18 (m, 2H, aromatic H on arenethiolate), 7.66 (m, 2H, terpyridyl H's), 8.29 (m, 6H, terpyridyl H's), 8.45 (t, 1H, $J = 7.5$ Hz, terpyridyl H), 8.96 (d, 2H, $J = 5.8$ Hz, terpyridyl H's). Positive ESI-MS: m/z 597 [M $-$ PF$_6$]$^+$. Anal. Calcd for C$_{23}$H$_{20}$N$_3$O$_2$SPtPF$_6$: C, 37.20; H, 2.70; N, 5.66. Found: C, 37.65; H, 2.61; N, 5.67.

Physical Measurements and Instrumentation. UV/vis spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer, and steady-state excitation and emission spectra were obtained on a Spex Fluorolog 111 spectrofluorometer. ^{1}H NMR spectra were recorded on a Bruker DPX-300 FT-NMR spectrometer (300 MHz) in CD$_3$CN at 298 K, and chemical shifts are reported relative to Me$_4$Si. Positive ESI mass spectra were recorded on a Finnigan LCQ mass spectrometer. Elemental analyses of the new complexes were performed on a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences.

The electronic absorption spectral titration for binding constant determination was performed with a Hewlett-Packard 8452A diode array spectrophotometer at 25 °C, which was controlled by a Lauda RM6 compact low-temperature thermostat. Supporting electrolyte (0.1 mol dm^{-3} ^{n}Bu$_4$NPF$_6$) was added to maintain a constant ionic strength of the sample solution in order to prevent any changes arising from a change in the ionic strength of the medium. Binding constants for 1:1 complexation were obtained by a nonlinear least-squares fit[12] of the absorbance (X) vs the concentration of the metal ion added (c_M) according to

$$X = X_0 + \frac{X_{\mathrm{lim}} - X_0}{2c_0}[c_0 + c_M + 1/K_S - [(c_0 + c_M + 1/K_S)^2 - 4c_0c_M]^{1/2}] \quad (1)$$

where X_0 and X are the absorbances of complex **1** at a selected wavelength in the absence and presence of the metal cation, respectively, c_0 is the initial concentration of complex **1**, c_M is the concentration of the metal cation M^{n+}, X_{lim} is the limiting value of absorbance in the presence of excess metal ion, and K_S is the stability constant.

For systems involving **1**:M^{n+} complexation in both 1:1 and 2:1 complexation stoichiometry, the binding constants were determined by using eq 2 based on the following derivations.

$$K_{11} = \frac{[\mathbf{1}\cdot \mathrm{M}^{n+}]}{c_1c_M}$$

$$K_{21} = \frac{[\mathbf{1}_2\cdot \mathrm{M}^{n+}]}{[\mathbf{1}\cdot \mathrm{M}^{n+}]c_1}$$

$$c_T = c_1 + [\mathbf{1}\cdot \mathrm{M}^{n+}] + [\mathbf{1}_2\cdot \mathrm{M}^{n+}]$$

$$c_T = \frac{[\mathbf{1}\cdot \mathrm{M}^{n+}]}{K_{11}c_M} + [\mathbf{1}\cdot \mathrm{M}^{n+}] + \frac{K_{21}[\mathbf{1}\cdot \mathrm{M}^{n+}]^2}{K_{11}c_M}$$

$$[\mathbf{1}\cdot \mathrm{M}^{n+}] = \frac{a}{2K_{21}};$$

$$a = -1 - K_{11}c_M + \sqrt{(1 + K_{11}c_M)^2 + 4K_{21}K_{11}c_Mc_T}$$

$$c_1 = \frac{a}{2K_{21}K_{11}c_M}$$

$$[\mathbf{1}_2\cdot \mathrm{M}^{n+}] = \frac{a^2}{4K_{21}K_{11}c_M}$$

$$X = \frac{X_0}{c_T}c_1 + \frac{X_{\mathrm{lim}}}{c_T}[\mathbf{1}\cdot \mathrm{M}^{n+}] + \frac{2X_{\mathrm{lim}}}{c_T}[\mathbf{1}_2\cdot \mathrm{M}^{n+}] \quad (2)$$

where c_1 is the concentration of complex **1** in the unbound state, c_T is the total concentration of platinum complexes, which is equal to the initial concentration of complex **1** (c_0), [**1**·M^{n+}] and [**1**$_2$·M^{n+}] are the concentrations of the 1:1 and 2:1 ion-bound adduct, respectively, and K_{11} and K_{21} are the stability constants for 1:1 and 2:1 complexation.

Crystal Structure Determination. Single crystals of **1** were obtained by vapor diffusion of diethyl ether into an acetonitrile solution of the complex.

Crystal data for **1**. [(C$_{29}$H$_{30}$N$_3$SO$_5$Pt)$^+$PF$_6$$^-$], formula weight = 872.69, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.946(2)$ Å, $b = 10.305(3)$ Å, $c = 16.948(4)$ Å, $\alpha = 76.11(2)°$, $\beta = 75.43(2)°$, $\gamma = 69.58(2)°$, $V = 1553(1)$ Å^3, $Z = 2$, $D_c = 1.866$ g cm^{-3}, μ(Mo Kα) = 46.98 cm^{-1}, $F(000) = 856$, $T = 301$ K. A purple crystal of dimensions 0.30 mm × 0.07 mm × 0.05 mm mounted on a glass fiber was used for data collection at 28 °C on a Rigaku AFC7R diffractometer with graphite monochromatized Mo Kα radiation ($\lambda = 0.710\,73$ Å) using $\omega-2\theta$ scans with an ω-scan angle of $(0.73 + 0.35 \tan \theta)°$ at a scan speed of 8.0 deg min^{-1} (up to six scans for reflection with $I < 15\sigma(I)$). Unit cell dimensions were determined on the basis of the setting angles of 25 reflections in the 2θ range of 21.8$-$25.9°. Intensity data (in the range of $2\theta_{\max} = 50°$; $h = -11$ to 11; $k = 0$ to 12; $l = -19$ to 20; three standard reflections measured after every 300 reflections showed decay of 1.66%) were corrected for decay and for Lorentz and polarization effects, and empirical absorption corrections were based on the ψ-scan of five strong reflections (minimum and maximum transmission factors of 0.747 and 1.000, respectively). A total of 5809 reflections were measured, of which 5474 were unique and $R_{\mathrm{int}} = 0.034$. A total of 4387 reflections with $I > 3\sigma(I)$ were considered observed and used in the structural analysis. The space group was determined on the basis of a statistical analysis of intensity distribution, and the successful refinement of the structure was solved by Patterson methods and expanded by Fourier methods (PATTY)[13] and refinement by full-matrix least squares using the software package TeXsan[14] on a Silicon Graphics Indy computer. One crystallographic asymmetric unit consists of one formula unit. The F atoms of the anion were disordered and were placed at 14 positions with F(1), F(1′), F(2), F(2′), F(3), F(4), F(5), F(6), F(7), F(8), F(9), F(10), F(11), and F(12) having occupation numbers of 0.56, 0.44, 0.56, 0.44, 0.49, 0.32, 0.41, 0.41, 0.49, 0.43, 0.39, 0.29, 0.33, and 0.44, respectively. In the least-squares refinement, all 39 non-H atoms of the complex cation and the P atom of the anion were refined anisotropically, the 14 disordered F atoms were refined isotropically, and 30 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. Convergence for 417 variable parameters by least-squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.028F_o^2)^2]$ for 4387 reflections with $I > 3\sigma(I)$ was reached at $R = 0.034$ and wR = 0.042 with a goodness of fit of 1.48. The quantity $(\Delta/\sigma)_{\max}$ is equal to 0.04 except for the disordered F atoms. The final difference Fourier map was featureless, with maximum positive and negative peaks of 0.95 and 1.80 e Å^{-3}, respectively.

Results and Discussion

Reaction of [Pt(trpy)Cl]Cl·2H$_2$O and 4′-mercaptomonobenzo-15-crown-5 in water in the presence of sodium hydroxide at

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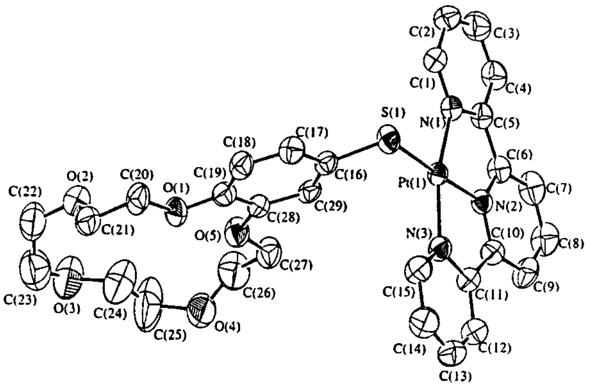

Figure 1. Perspective drawing of the complex cation of **1** with atomic numbering. Thermal ellipsoids are shown at the 40% probability level.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for Complex **1**

Pt(1)−N(1)	2.026(5)	N(1)−Pt(1)−N(2)	80.5(2)
Pt(1)−N(2)	1.969(5)	N(2)−Pt(1)−N(3)	80.8(2)
Pt(1)−N(3)	2.023(6)	N(1)−Pt(1)−N(3)	161.2(2)
Pt(1)−S(1)	2.313(2)	N(2)−Pt(1)−S(1)	178.1(2)
		N(1)−Pt(1)−S(1)	98.3(2)
		N(3)−Pt(1)−S(1)	100.4(2)
		Pt(1)−S(1)−C(16)	109.4(2)

40 °C followed by metathesis reaction using $^{n}\mathrm{Bu_4NPF_6}$ and subsequent recrystallization from MeCN−Et$_2$O afforded [Pt(trpy)(S-benzo-15-crown-5)]PF$_6$, **1**, as purple crystals. The crown-free analogue [Pt(trpy)(SC$_6$H$_4$ -(OMe)$_2$-3,4)]PF$_6$, **2**, was also synthesized using similar methods. The identity of the complexes have been confirmed by satisfactory elemental analyses, ^{1}H HMR spectroscopy, and ESI-MS. The crystal structure of [Pt(trpy)(S-benzo-15-crown-5)]PF$_6$, **1**, has also been determined.

X-ray Crystal Structure Determination. Figure 1 depicts the perspective drawing of the complex cation of **1** with atomic numbering. Selected bond distances and angles for **1** are summarized in Table 1. The coordination geometry is essentially square planar in which the distance of Pt to the inner N atom of the terpyridine ligand is significantly shorter than those of Pt to the other two outer N atoms. This is commonly observed in typical platinum(II) terpyridine complexes.[1d,2i,3e] The deviations of the N(1)−Pt−N(2) and N(2)−Pt−N(3) bond angles from the idealized 90° and that of N(1)−Pt−N(3) from 180° are a result of the bite angles set by the terpyridine ligand, as required by the steric demand of the terpyridyl group, typically obtained in platinum(II) terpyridyl systems.[1d,2i,3e] The bond length of Pt−S is 2.313(2) Å, and the S−Pt−N(1), S−Pt−N(2), and S−Pt−N(3) angles are 98.3(2)°, 178.1(2)°, and 100.4(2)°, respectively. These are comparable to those found in other Pt(II) terpyridyl thiolate complexes.[3e,4a] An intermolecular Pt···Pt distance of 4.3908 Å suggested that there was no significant intermolecular interaction between the two metal centers.

Electronic Absorption. The electronic absorption spectrum of **1** in acetonitrile shows intense vibronic-structured absorption at 300−350 nm, which is characteristic of the intraligand (IL) transition of terpyridine ligands. Besides the IL transitions, a low-energy broad absorption band at 572 nm is observed. The occurrence of this band at such a low energy suggests that it is unlikely metal-to-ligand charge transfer (MLCT) in character. In view of the good electron-donating behavior of the thiolate group and with reference to previous spectroscopic work on platinum(II) complexes containing diimine and aromatic thiolate ligands,[3a,c−e] the low-energy absorption is tentatively assigned as the $p_\pi(RS^-) \rightarrow \pi^*$(trpy) ligand-to-ligand charge transfer (LLCT) transition. A similar LLCT assignment has also been suggested for a related [Pt(terpy)(NS)]ClO$_4$ complex (NS = pyridine-2-thiolate),[3e] in which a higher energy band at 520 nm was observed. The lower absorption energy of **1** compared with that of [Pt(terpy)(NS)]ClO$_4$ is in line with an assignment of a LLCT transition because the presence of an electron-donating polyether ring on the thiolate ligand increases the electron richness of the thiolate group and raises the $p_\pi(RS^-)$ orbital energy. Complex **1** has been found to be nonemissive both in fluid solution and in the solid state.

Cation Binding Studies. Upon addition of alkali or alkaline earth metal ions to a solution of **1** in acetonitrile (0.1 mol dm^{-3} $^{n}\mathrm{Bu_4NPF_6}$), the LLCT absorption band shows a blue shift in energy with well-defined isosbestic points. UV−visible spectral changes of **1** (5.2×10^{-4} mol dm^{-3}) upon addition of sodium perchlorate were observed (Figure S1 of Supporting Information). Similar shifts were not observed in a control experiment using the crown-free complex [Pt(trpy)(SC$_6$H$_4$-(OMe)$_2$-3,4)]PF$_6$, **2**, indicating that these shifts were ascribed to the binding of the cations to the polyether cavity. For Na$^+$, a log K_S of 4.01 (±0.02) was obtained according to eq 1. The close agreement of the experimental data with the theoretical fit (Figure S1 inset of Supporting Information) is supportive of a 1:1 stoichiometry. This 1:1 binding mode has further been confirmed by the method of continuous variation,[15] as seen from a Job's plot where a mole fraction **1**/(**1** + Na$^+$) of close to 0.5 is observed (Figure S2 of Supporting Information). The 1:1 stoichiometry and the large binding constant obtained are in accordance with the well-known binding mode of benzo-15-crown-5 for sodium ions with its appropriate cavity size.[16] For K$^+$, the lack of well-defined isosbestic points in the UV−visible spectral change and the absence of a satisfactory fit to eq 1 suggested that both complexes with stoichiometries of 2:1 (**1**:K$^+$) and 1:1 were formed. According to eq 2, log K_{11} and log K_{21} values of 3.30 (±0.04) and 2.93 (±0.04), respectively, were obtained. The close resemblance of the experimental data to that of the theoretical fit to eq 2 is supportive of such a binding model (Figure S3 of Supporting Information). A similar 2:1 sandwich binding mode has been commonly observed in other K$^+$-(benzo-15-crown-5) systems.[7d,17] In the case of Ba^{2+}, no isosbestic points occurred in the UV−visible spectral change at low concentrations. However, as the concentration of Ba^{2+} was further increased, a well-defined isosbestic point appeared. Presumably, complexation of a Ba^{2+} ion to complex **1** was in a 1:2 ratio at low Ba^{2+} ion concentration but in a 1:1 ratio in the high Ba^{2+} ion concentration regime. Attempts to obtain the binding constants were unsuccessful because no satisfactory fit to eq 2 could be obtained. It is likely that the binding process might not be as simple as we thought. As a result, only the stoichiometry of 1:1 complexation was considered and a log K_S of 2.84 (±0.08) was roughly estimated by employing the data in the concentration range where the isosbestic point exists and fitting them to eq 1.

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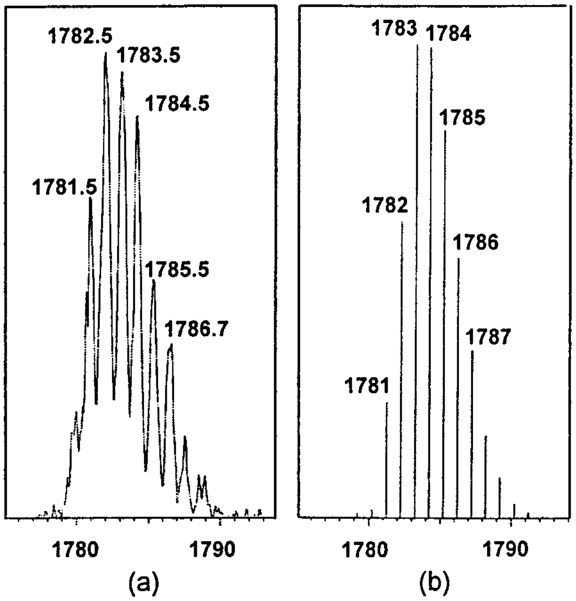

Figure 2. (a) Ion cluster at *m*/*z* 1783, expanded from the positive-ion ESI-mass spectrum in acetonitrile solution. (b) Simulated isotope pattern for the adduct $\{\{[Pt(trpy)(S\text{-benzo-15-crown-5})]_2{\cdot}K\}(PF_6)_2\}^+$.

The ion-binding studies have further been confirmed by ESI-MS. For both Na^+ and Ba^{2+} cation binding studies, only the 1:1 adduct of the bound species was observed under the experimental conditions used, while for K^+, both 1:1 and 2:1 adducts were observed. Figure 2a illustrates the ion cluster at *m*/*z* 1783, attributed to the 2:1 sandwiched species $\{\{[Pt(trpy)(S\text{-benzo-15-crown-5})]_2{\cdot}K\}(PF_6)_2\}^+$. The isotopic pattern of the expanded ion cluster is fully consistent with the simulated one (Figure 2b). Similar to the absorption studies, a control experiment with crown-free analogue **2** did not show the presence of such ion-bound species upon the addition of metal ions, providing further supporting evidence for the binding of cations to the crown moieties. It is interesting to note that the stacked form of **1**, $\{[Pt(trpy)(S\text{-benzo-15-crown-5})]_2(PF_6)\}^+$, has also been shown to be present in minute quantities in solution at moderate to high concentrations, as evidenced by the observation of the ion cluster at *m*/*z* 1599. The occurrence of such stacked aggregates of **1** is not surprising in view of the strong propensity of square planar metal polypyridine complexes to form both weak metal−metal bonding and $\pi-\pi$ stacking interactions.[2] Attempts to determine the association constant *K* for the dimerization and oligomerization processes using UV−vis spectral studies were unsuccessful because no apparent deviation from Beer's law was observed in the low-energy absorption band (in the range $10^{-4}-10^{-2}$ mol dm^{-3}), probably as a result of its predominant LLCT character and the small *K* value expected for monocationic species.

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Supporting Information Available: Figure S1 showing the electronic absorption spectrum of **1** in acetonitrile (0.1 mol dm^{-3} $^nBu_4NPF_6$) upon addition of $NaClO_4$, with an inset showing a plot of absorbance vs $[Na^+]$ monitored at $\lambda = 625$ nm, Figure S2 showing Job's plot for the binding of **1** with Na^+ ions, Figure S3 showing a plot of absorbance vs $[K^+]$ monitored at $\lambda = 630$ nm, and tables giving atomic coordinates, anisotropic thermal parameters, bond lengths, and bond angles for complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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